What is d-Limonene?

d-Limonene: The Safe Citrus Solvent from Florida Ch

D-LIMONENE:
A CLEANER FROM NATURE

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d-Limonene is the major component of the oil extracted from citrus rind. When citrus fruits are juiced, the oil is pressed out of the rind. This oil is separated from the juice, and distilled to recover certain flavor and fragrance compounds. The bulk of the oil is left behind and collected. This is food grade d-limonene. After the juicing process, the peels are conveyed to a steam extractor. This extracts more of the oil from the peel. When the steam is condensed, a layer of oil floats on the surface of the condensed water. This is technical grade d-limonene.

In the past decade, the use of d-limonene has expanded tremendously. Much of the product goes into making paint solids, used to impart an orange fragrance to products, and used as a secondary cooling fluid. But the largest growth segment has been the use of d-limonene in cleaning products. This has occurred in both industrial uses and in household/institutional products. d-Limonene can be used either as a straight solvent, or as a water dilutable product.

As a straight solvent, d-limonene can replace a wide variety of products, including mineral spirits, methyl ethyl ketone, acetone, toluene, glycol ethers, and of course fluorinated and chlorinated organic solvents. As with most organic solvents, d-limonene is not water soluble, so it can be used in the typical water separation units. With a KB value of 67, d-limonene has solubility properties close to that of CFC's, indicating that it is a much better solvent than a typical mineral spirit. Straight d-limonene can be used as a wipe cleaner, in a dip bath, or in spray systems as a direct substitute for most other organic solvents.

By combining d-limonene with a surfactant package, a water dilutable and rinsible solution can be made. In most cases these products are used in the institutional and household settings in place of caustic and other water based cleaners. A concentrated solution of a d-limonene/surfactant solution can be made to be diluted before use, or pre-diluted solutions can be formed. The use concentrations of d-limonene in these situations are usually 5-15%. In general these solutions are used as spray and wipe cleaners. The water dilutable solutions can also be used in industrial settings where a water rinse of the parts is desired to remove any residue which may remain.

d-Limonene is a very versatile chemical which can be used in a wide variety of applications. It is extremely safe and more effective than typical cleaning solutions.

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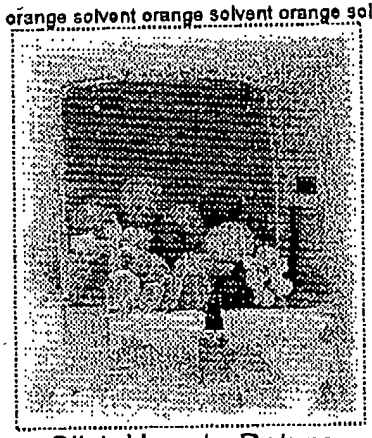

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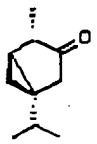
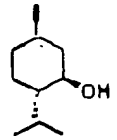
Terpenes

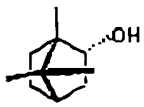
3. Terpenes

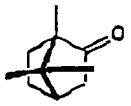
Many natural products, other than alkaloids, show medicinal properties or biological activity. Among these are compounds which fall in the general class of terpenes, compounds made up of 5-carbon units, often called isoprene units, put together in a regular pattern, usually head-to-tail in terpenes up to 25 carbons. Terpenes containing 30 carbons or more are usually formed by the fusion of two smaller terpene precursors such that the head-to-tail "rule" appears to be violated.

Menthol, a monoterpene (10 carbons) isolated from various mints, is a topical pain reliever and antipuretic (relieves itching). Plants in the mint family have been used for medicinal purposes since before 2000 BC, but menthol was not isolated until 1771. Thujone, another monoterpene, is the toxic agent found in *Artemisia absinthium* (wormwood) from which the liqueur, absinthe, is made. Borneol and camphor are two common monoterpenes. Borneol, derived from pine oil, is used as a disinfectant and deodorant. Camphor is used as a counterirritant, anesthetic, expectorant, and antipruritic, among many other uses.

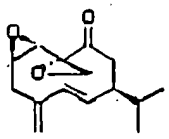

thujone

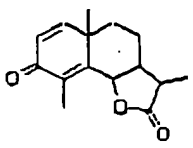

menthol

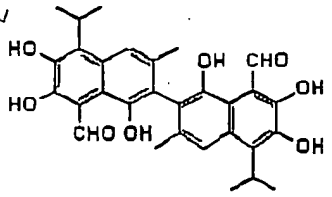

(+)-borneol

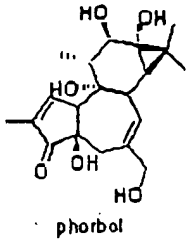

(+)-camphor

Periplanone B, a sesquiterpene (15 carbons), is the female sex attractant of a species of cockroach. Another sesquiterpene, santonin, is also found in wormwood and is a photosensitizer. Gossypol is a dimeric sesquiterpene isolated from the seeds of cotton plants. It has been used clinically in China as a male contraceptive.


periplanone

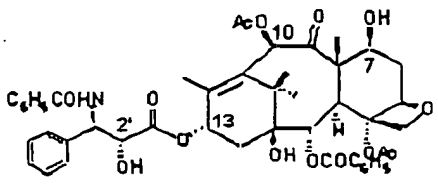

santonin

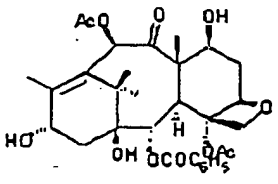

gossypol

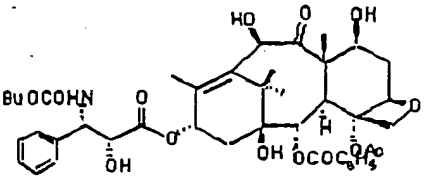

phorbol

Commonly used ornamental plants, particularly when they have a tropical origin, often contain biologically active compounds. Many of the Euphorbiaceae contain potent skin irritants derived from phorbol in their latex. Phorbol, a diterpene (20 carbons), is known as a cocarcinogen, a compound that is not carcinogenic but which promotes carcinogenesis in the presence of another agent.

One of the most well-known medicinally valuable terpenes is the diterpene, taxol. Taxol was first isolated from the bark of the Pacific yew, *Taxus brevifolia*, in the early 1960's, but it was not until the late 1980's that its value as an anticancer drug was determined. It acts to stabilize the mitotic apparatus in cells, causing them to act as normal cells rather than undergo rapid proliferation as they do in cancer. There has been a great deal of interest in taxol from the standpoint of understanding what pieces of the compound are required for activity. These structure-activity relationships have been determined by isolating or synthesizing homologues and derivatives of taxol and testing these compounds for their anti-cancer activity in various cell culture and *in vivo* screens. If the side chain ester was removed to give baccatin III, activity was lost. If different N-acyl groups were present on the side chain, activity was maintained. If the 2'-OH on the side chain was converted to another group, activity was reduced unless the group could be hydrolyzed *in vivo*. The stereochemistry at C-7 has no effect on the activity, nor is C-10 acylation critical. The oxetane ring must be present.

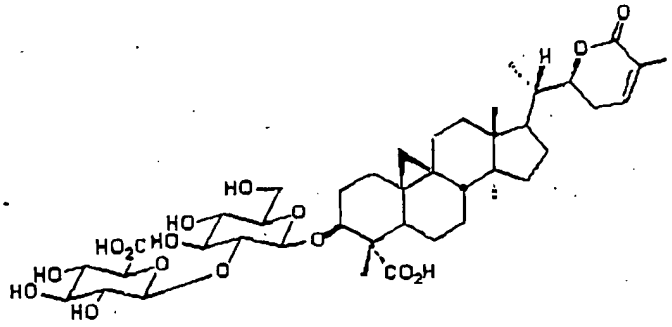

taxol


baccatin III

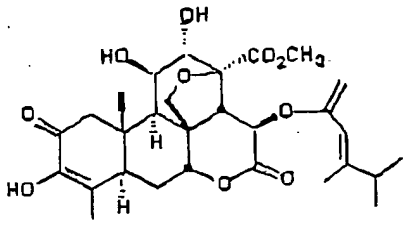

taxotere

Since one of the major problems with taxol, as with many other natural products used as drugs, is solubility in

aqueous systems, much effort has been devoted to finding a more soluble form. Taxotere (docetaxel) was prepared by the French firm, Rhone-Poulenc, and has similar activity to taxol (paclitaxel), but slightly better solubility. Other researchers have tried to add a group to the 2'-OH which would increase the solubility and then be removed *in vivo*. These are mostly esters with a salt incorporated to increase the water solubility. Other investigators have modified the C-13 side chain ester and added functionality at C-14 to increase the oral bioavailability. These modified taxoids are still at early stages of testing, but illustrate the principles o development of second generation drugs. In these circumstances, the SAR studies have been used to guide the modification of the natural product to maintain or improve the activity while adjusting the physical properties.



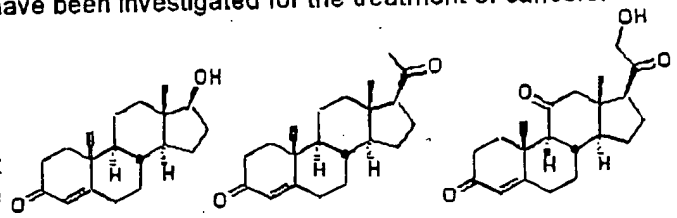
Arbruside E



bruceantin

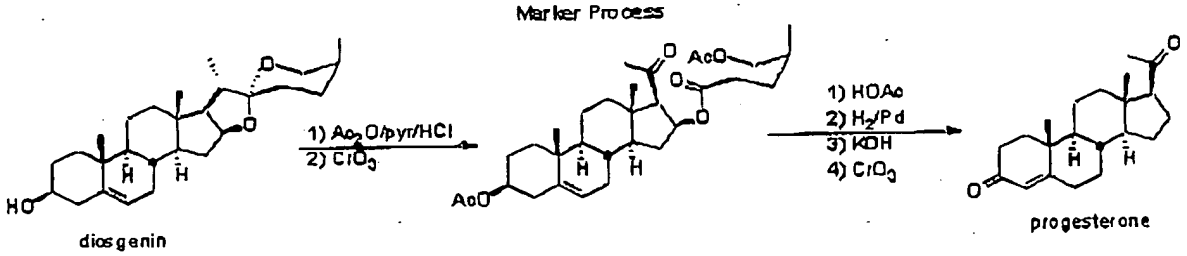
Triterpenes contain 30 carbons, derived essentially from coupling of two sesquiterpene precursors. Many of these compounds occur in plants as glycosides, often called saponins (molecules made up of sugars linked to steroids or tripterpenes) due to their ability to make aqueous solutions appear foamy. Arbruside E, for example, comes from a plant called *Arbrus precatorius* (jequerity) which has been used as an abortifacient and purgative. Arbruside E, however, appears to be relatively non-toxic, and is 30-100 times sweeter than sucrose, making it a potential sugar substitute. Triterpenes of the quassinoid class, such as bruceantin, have been shown to have significant antineoplastic activity in animal systems and have been investigated for the treatment of cancers.

Steroids are modified triterpenes. They are probably most familiar from their role as hormones, *i.e.*, androgens such as testosterone and estrogens such as progesterone. Steroids, such as cortisone, are most often used as anti-inflammatory agents, but many have other uses such as in birth control pills. Prior to 1943, most steroids were obtained from natural sources. For example, progesterone could only be isolated in quantities of 20 mg from 625 kg of pig ovaries. The large numbers of commercially and medicinally valuable steroids available today have been made possible by the semi-synthetic preparation of progesterone from diosgenin. This process, known as the Marker process, was developed in the early 1940's by Russell Marker, a rather colorful character, who left his position of professor o chemistry at Penn State to pursue this project in Mexico. Marker collected Mexican yams in bandit country, processed the yams to isolate the diosgenin, and then converted the diosgenin into *ca.* 3 kg of pure progesterone at a cost of $8 per gram. He and a Mexican pharmacist then formed a company which later became the major pharmaceutical company, Syntex.



testosterone progesterone cortisone

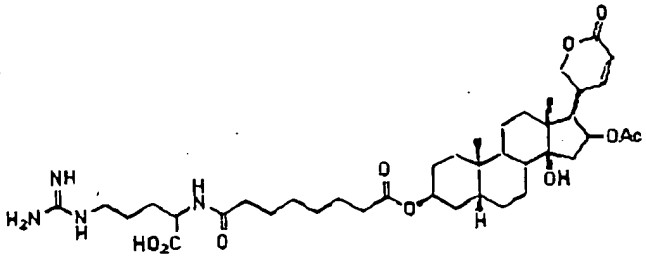
Marker Process



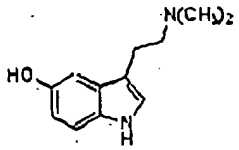
diosgenin progesterone

Other steroidal compounds play different roles. Digitoxin, one of the components of the heart drug digitalis, is called a cardiac

glycoside and is classed as a steroid. Digitalis is actually the powdered leaves of *Digitalis purpurea*, also known as foxglove. Excessive use of digitalis has been known to produce xanthopsia (yellow vision). Related steroids, *e.g.*, bufotoxin isolated from *Bufo marinus* (the cane toad), are actually more toxic than useful. The cane toad also produces bufotenine, a substance close in structure to dimethyltryptamine and the hallucinogenic alkaloids of ergot.



bufotoxin



bufotenine

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